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(54) PROCESS AND APPARATUS FOR THE ISOLATION OF
AROMATIC POLYMERS

(71) We, INVENTA A.G. FÜR FORSCHUNG UND PATENTVERWERTUNG, ZÜRICH, of Stampfenbachstrasse 38, Zurich, Switzerland, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a process for isolating aromatic polymers from solution and to apparatus suitable for use in this process. The invention is applicable to any aromatic polymer comprising recurring benzene rings each adjacent pair of which are linked in the 1,3- or 1,4-positions either by direct bonds or by —O— or —S— atoms or —SO₂—, —CO—, —CONH—, —N=N—, —(CH₂)_n— (n = 1 or 2) or —C(CH₃)₂— groups. Often the aromatic polymers have recurring units of the formula —Aw(Ax)_p(Ay)_q(Az)_r— (formula (I)) where p, q and r may be the same or different and are zero or 1, each A represents a benzene ring and w, x, y and z represent linkages in the 1,3- or 1,4-positions and which may be the same different and may be direct bonds or —O— or —S— atoms or —SO₂—, —CO—, —CONH—, —N=N—, —(CH₂)_n— (n = 1 or 2) or —C(CH₃)₂— groups.

High molecular weight aromatic polymers of the type described have acquired considerable industrial interest in consequence of their outstanding sustained thermal stability. Commercially they are usually made by polycondensation of suitable bifunctional starting materials in polar aprotic solvents in which the polymers formed are soluble. In some cases, for example, that of the aromatic polyamides, in which w, x, y and z are —CONH— in formula (I), salts, for instance, lithium chloride or calcium chloride must be added in order to keep the polymers formed in solution.

Prior to finally forming the polymers into commercially usable products, such as injection-moulded articles, films, coatings, fibres and continuous sections, the polar aprotic solvents and any added salts must be removed completely from the polymer. If this is not done the properties in use of the final products are appreciably impaired, in particular if the products are used at high ambient temperatures.

Tests such as have been described, for example, in U.S. Patent Specification 3,360,598 have shown that a salt content of 0.1% or above in aromatic polyamides may be sufficient to impair the mechanical properties of fibres produced from them. Similarly a residual solvent content impairs the properties of formed or shaped products. For example a residual solvent content of above 0.5% may result in premature discolouration and embrittlement of the products when they are heated to service temperatures of 150—180°C.

The removal of residual solvents or salts from aromatic polymers is rendered difficult by the fact that the polymers have a high affinity for polar aprotic solvents and alkali metal or alkaline-earth metal halide salts and obstinately retain them. This is the reason why conventional extraction or drying methods conducted on the polymers in granular or coarse powder form have not been successful or have succeeded only after an economically unacceptable number of washing operations.

In recognition of these difficulties, it has been proposed in German Patent Specification 2,200,502 to operate with a high-melting auxiliary solvent in the isolation of aromatic polymers. After the addition of the auxiliary solvent, the reaction solvent is distilled off *in vacuo* and the solution of the polymer in the auxiliary solvent which

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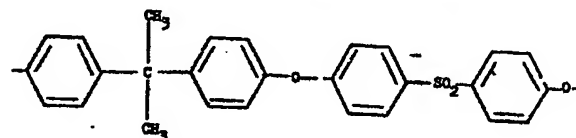
is left behind is caused to solidify by pouring on to metal sheets, comminuted, ground and finally extracted with a third, low-boiling organic solvent. In this way, the aromatic polymer is obtained in the form of powder, which is lastly subjected in addition to extraction with water. This process is complicated and time-consuming, and in any event we are unaware of any analytical proof showing that no auxiliary solvent is left in the polymer by this method.

We have now devised a new separation method for aromatic polymers, and preferably for aromatic polymers of formula 1, which is effective for separating the polymers from salts and residual solvents and which results in the polymer being isolated in powder form, the powder conveniently being in fine homogeneous form.

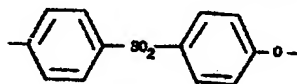
The process of the invention comprises spraying the polymer in solution in polar aprotic solvent under pressure onto the surface of a moving liquid precipitating medium of the formula ROH where R represents hydrogen or C₁₋₄ alkyl. The polymer precipitates in the medium and the precipitate can be collected in powder form in any convenient manner.

We list below various known combinations of aromatic polymers and polar aprotic solvents that can be used in the invention but it will be appreciated that the listed solvents can be used for other polymers and the listed polymers can be dissolved in other solvents. The examples are:

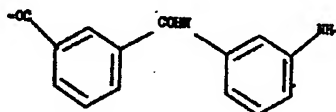
a solution of a polymer having recurring structural units



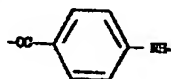
in dimethyl sulphoxide (Swiss Patent Specification 447,603);
a solution of a polymer having recurring structural units



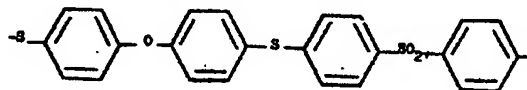
in sulpholan (British Patent Specification 1,153,035);
a solution of a polymer having recurring structural units



in dimethyl acetamide with the addition of calcium chloride (U.S. Patent Specification 3,063,966) or in N-methylcaprolactam without the addition of salt (Belgian Patent Specification 4,779,192);
a solution of a polymer having recurring structural units



in tetramethylurea with the addition of lithium chloride (U.S. Patent Specification 3,671,542);
a solution of a polymer having recurring structural units



in dimethylformamide (British Patent Specification 1,124,200);

a solution of an internal copolymer without regular structural units prepared from 4-mercaptophenol and 4,4'-dichlorodiphenylsulphone in sulpholan (German Patent Specification 2,117,820).

Other examples of polymer solutions which are suitable for the present process will be apparent from, for example, the patent specifications mentioned.

If necessary or desired a mixture of polar aprotic solvents can be used. Also if necessary or desired a diluent can be included in the solution, for example to reduce the viscosity of the solution. If a diluent is to be used then dimethyl formamide is often suitable, particularly when water is to be used as the precipitating medium.

Water is preferably employed as the precipitating medium but sometimes it is desirable to use methanol or ethanol.

To achieve good results the viscosity of the solution being sprayed is important. Preferably the viscosity is between 1 and 100 poise, advantageously between 5 and 20 poise. The viscosity of a polymer solution is dependent on the molecular weight of the dissolved polymer, the concentration and the temperature. However in order to obtain the desired physical properties of the polymer the molecular weight generally cannot be varied too much and generally must not be below certain minimum values, generally 10,000—15,000. As a result the viscosity of the solution can in practice be adjusted only by varying the concentration of the polymer or by varying the temperature of the solution. The latter course is preferred, since the viscosity depends to a high degree on the temperature, as a result of which the desired viscosity range can be obtained without the use of large amounts of solvents or diluents. It is therefore preferred to spray the polymer solution at elevated temperature between 50° and 150°C in a viscosity range of 5—20 poise.

Polymer solution can be sprayed in a stream of compressed air by producing in a tube, which is preferably arranged horizontally, a powerful air stream which sweeps past the upper end of a preferably vertically arranged tube dipping into the polymer solution and serving as an exit conduit. This is the working principle of a conventional, compressed-air-operated paint spray gun. This method has numerous disadvantages including high air consumption per kg of polymer solution delivered, high solvent losses and non-uniform size of the drops in the spraying jet. Accordingly this method is not very satisfactory for use in the invention and instead it is strongly preferred to spray purely by liquid pressure, the above listed disadvantages being avoidable provided suitable nozzles are used.

The liquid pressure is preferably 50—300 atmospheres gauge and this can be produced in various ways, for example by means of piston, diaphragm or geared pumps, or by applying the pressure of an inert gas with the necessary intensity to a supply vessel containing the polymer solution. The pump and supply vessel are preferably surrounded by a double jacket through which circulates a heating medium which brings the entire spraying apparatus to the desired temperature. The pump and the high-pressure supply vessel are connected via a hose or a pipe to the nozzle, from which the spray jet issues and strikes the moving surface of the precipitating medium from a distance of, preferably, 20—60 cm.

The moving surface of the precipitating medium is preferably a smooth surface and may be one at which substantially or wholly laminar flow occurs. Any convenient smooth moving surface may be used in the invention. In one form the surface may be the surface of a moving film, for example a sheet or cylindrical film. In another, the surface may be the moving surface of a bulk volume of the medium and conveniently this can be achieved by providing a forced vortex of the medium having a smooth parabolic surface.

Apparatus suitable for use in the process of the invention comprises a first supply vessel that may contain the precipitant medium, means in or associated with the first supply vessel for providing a moving surface of the medium, a second supply vessel that may contain the polymer solution, an atomizer nozzle for spraying the solution onto the moving surface, and a high pressure pump for delivering the solution to the moving surface.

Suitable apparatus is illustrated in the accompanying drawings in which Figure 1 shows diagrammatically the entire apparatus while Figures 2 and 3 show diagrammatically the part of the apparatus where the solution is sprayed onto the moving surface.

Referring to Figure 1, the apparatus comprises a supply vessel 1 for the polymer solution, a high pressure pump 2, a heated pipe 3 leading to a spray nozzle 4, a supply vessel 5 containing the precipitating medium (often water), a stirring apparatus 6 powered from beneath the vessel and designed to provide the desired moving surface

in the vessel 5, a discharge pipe 7 leading from the vessel to a centrifuge, a heating oil circulating pump 8 and a heat exchanger 9.

When, as in Figure 1, a rotating cone of the medium is employed as the moving surface a nozzle which sprays the polymer solution in the form of a complete or solid cone is used with advantage. The process can be rendered continuous by making up for the mixture of polymer powder and solvent/precipitant running off at 7 by adding pure precipitant to the vessel 5, so that the same liquid level is always maintained.

Other continuous methods of carrying the invention into effect are illustrated in Figures 2 and 3. In Figure 2, a film 10 of precipitant runs out of a slit nozzle 11 over an inclined surface 12 and is sprayed with the polymer solution through a flat-jet nozzle 13. According to Figure 3, a film 14 of precipitant is produced on the inner surface of a cylindrical vessel 15 by means of an annular slit nozzle 16 and the polymer solution is sprayed by means of hollow cone nozzle 17.

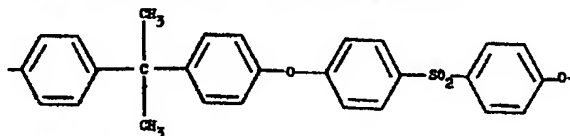
Nozzles capable of supplying the desired form of jet spray are well known. Whilst they were probably designed initially for other purposes, for instance for spraying water, salt solutions, dye dispersions or lacquer solutions, they are suitable for the present purpose, provided that operation is conducted in a substantially higher pressure range of 50—300 atmospheres gauge.

The aromatic polymer powder produced in the process is obtained as a dispersion in the solvent/precipitant mixture, from which it may be separated by centrifuging or filtration. The powder has a restricted particle size distribution such as cannot be achieved by other methods, such as, for instance compressed-air spraying. The average particle size depends on the concentration, viscosity and temperature of the polymer solution, as well as the spraying pressure and the nozzle cross-section. Depending on the adjustment of these parameters, the average particle size of the powder can be varied approximately within the range of 10 to 300 nm. The individual particles of the powder have a large specific area, as a result of which subsequent washing and drying processes, in particular the extractive removal of residual solvents and salts, are greatly facilitated.

The following Examples serve to illustrate the invention more fully.

Example 1.

A solution of a polymer with recurring units of the structure



in dimethyl sulphoxide is prepared in accordance with Example 1 of Swiss Patent Specification 447,603 in an amount 100 times as large. The solution is diluted with 4.5 litres of dimethylformamide and filtered off from the suspended potassium chloride.

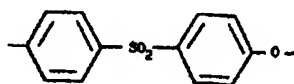
The solution is introduced into a 25-litre vessel of stainless steel (1 in Figure 1) and heated therein to 110°C. The viscosity of the solution at this temperature is 8.5 poise. A heated high-pressure piston pump delivers the solution at a pressure of 120 atmospheres gauge through a pipe likewise heated to 110°C to a nozzle producing a solid conical jet (Lechler Model SZ 006/45), from which the solution is sprayed.

The nozzle is arranged centrally in the upper part of a 100-litre vessel of stainless steel filled with 30 litres of water which is so stirred by means of a stirrer installed in the bottom of the vessel that a parabolic trough of water having a laminar flow is formed. The sprayed jet of polymer solution strikes the rotating surface of the water from a distance of 40—50 cm and the solid polymer is separated here in the form of a powder with an average particle size of 80 nm.

The powder is separated from the mixture of water and solvent by centrifuging, washed three times with hot water and dried. After washing and drying, the powder contains 0.1% of organic solvent and can be worked up directly into high-grade films in double screw extruders.

Example 2.

A solution of a polymer with recurring units of the structure



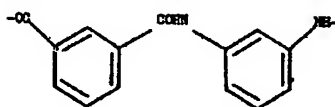
in sulpholan (tetrahydrothiophen-S,S-dioxide) is prepared in accordance with Example 12 of British Patent Specification 1,153,035 in an amount 500 times as large. The solution, which is diluted with 6 litres of dimethylformamide and filtered, is introduced into a 25-litre vessel of stainless steel and heated to 85°C. The viscosity of the solution at this temperature is 11 poise. A high-pressure diaphragm pump likewise heated to 85°C delivers the solution at a pressure of 145 atmospheres gauge to a swingable discharge nozzle, Schlick Model 655/1, with a spraying angle of 15°.

The isolation of the polymer in the form of a fine powder is performed in accordance with Figure 2, by the flat jet of atomised polymer solution striking a moving film of water from a distance of 40 cm, the film of water issuing from a slit nozzle with a size of 160 × 0.3 mm and running down over a surface inclined at 45°. The powder dispersion arrives by way of a funnel at the centrifuge, where the polymer powder is separated from the mixture of water and solvent. With continuous operation, this mixture is circulated until the concentration of solvent is about 20—30% by weight. From this time on, the concentration of solvent is kept constant by adding fresh water and the corresponding amount of liquid is withdrawn from the circuit.

The powder removed from the centrifuge has an average particle size of 120 nm and, after being boiled three times with water, is free from salts and solvents.

Example 3.

A solution of a polyamide with recurring units of the structure



in dimethyl acetamide, which contains 10% by weight of polyamide and 2% of calcium chloride referred to the solvent, is prepared in accordance with Example 14 of U.S. Patent Specification 3,063,966.

10 litres of this solution are introduced into a stock vessel with a capacity of 25 litres and heated to 70°C. The viscosity of the solution at this temperature is 18.6 poise. By means of a preheated high-pressure piston pump the solution is supplied at a pressure of 220 atmospheres gauge to a Lechler hollow cone nozzle, Type KS 1/13, with a spraying angle of 60°.

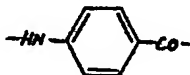
The precipitation of the polyamide powder is performed in accordance with Figure 3 in a cylindrical vessel with a diameter of 50 cm and a length of 100 cm and along the inner face of which a film of methanol which is continuous all round flows vertically downwards. The methanol film is produced by means of an annular slit nozzle with slit width of 0.3 mm mounted in the cover of the vessel. The methanol feed is 8 litres/min., while the polymer solution is sprayed at a rate of 2 litres/min.

A suspension of the polyamide powder is supplied to a continuously operating pusher centrifuge, in which the powder is separated from the mixture of methanol and dimethylacetamide. After boiling three times with methanol, the powder shows the following analytical data:

Average particle size	82 nm
Dimethyl acetamide content (by gas chromatography)	0.06%
Calcium chloride content (chlorine determination)	0.02%

Example 4.

A solution of a polymer with recurring units of the structure



in tetramethylurea, which contains 10.8% of polyamide and 6% of lithium chloride referred to the solvent, is prepared in accordance with Example 58 of U.S. Patent Specification 3,671,542 in an amount 10 times as large.

20 litres of this solution are sprayed and turned into powder in accordance with Example 1 in an apparatus according to Figure 1. The following operating conditions are used:

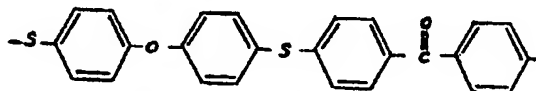
5	Temperature of the polymer solution	120°C	5
	Viscosity at 120°C	21.2 poise	
	Spraying pressure	240 atms. gauge	
	Nozzle	Spray systems 2/30	
	Spray jet	solid cone	
	Delivery	3.5 litres/min.	

Analytical data of the powder (after washing and drying):

10	Average particle size	105 nm	10
	Bulk weight	0.20	
	Tetramethylurea content	0.52%	
	Lithium chloride content	0.23%	

Example 5.

A solution of a polymer with recurring units of the structure



15 in dimethylformamide is prepared in accordance with Example 1 of British Patent Specification 1,124,200. 15

The isolation of the polymer in powder form is carried out in accordance with Example 3 in an apparatus according to Figure 3. The following operating conditions are used:

20	Temperature of the polymer solution	85°C	20
	Viscosity of the solution at 85°C	17.5 poise	
25	Spraying pressure	200 atms. gauge	25
	Nozzle	Lechler KS 1/13	
	Spray jet	Hollow cone	
	Spraying angle	60°	
	Delivery	3.9 litres/min.	

Analytical data of the powder after washing and drying:

30	Average particle size	70—80 nm	30
	Bulk weight	0.18	
	Dimethylformamide content	0.18%	

Example 6.

35 A solution of an aromatic polyetherthioether without regular structural units is prepared in dimethyl sulphoxide from monothiohydroquinone and 4,4'-dichlorodiphenylsulphone in accordance with Example 1 of German Patent Specification 2,117,820. 35

The solution, which is filtered and diluted with dimethyl sulphoxide to a polymer content of 18%, is sprayed to form powder in accordance with Example 3 in an apparatus according to Figure 3, the following operating conditions being used:

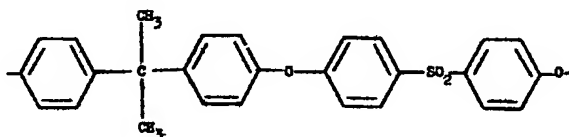
40	Temperature of the polymer solution	60°C	40
	Viscosity of the solution at 60°C	6.3 poise	
45	Spraying pressure	200 atms. gauge	45
	Nozzle	Schlick 103/3	
	Spray jet	Hollow cone	
	Spraying angle	45°	
	Delivery	4.5 litres/min.	

Analytical data of the powder after washing and drying:

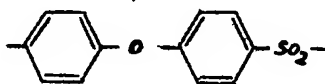
50	Average particle size	140 nm	50
	Bulk weight	0.16	
	Dimethyl sulphoxide content	0.12%	
	Sodium chloride content	0.02%	

WHAT WE CLAIM IS:—

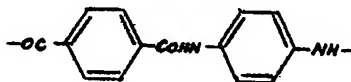
1. A process in which a high molecular weight aromatic polymer comprising recurring benzene rings each adjacent pair of which are linked in the 1,3- or 1,4-positions either by direct bonds or by a $-\text{O}-$ or $-\text{S}-$ atoms or a $-\text{SO}_2-$, $-\text{CO}-$, $-\text{CONH}-$, $-\text{N}=\text{N}-$, $-(\text{CH}_2)_n-$ ($n = 1$ or 2) or $-\text{C}(\text{CH}_3)_x-$ group, is isolated as a powder from solution in a polar aprotic solvent by spraying the solution under pressure onto the surface of a moving liquid precipitating medium of the formula ROH where R represents hydrogen or C_{1-4} alkyl.
2. A process according to claim 1 in which the polymer solution being sprayed has a viscosity of from 5 to 20 poise.
3. A process according to claim 1 or claim 2 in which the polymer solution being sprayed has a temperature of from 50 to 150°C.
4. A process according to any preceding claim in which the polymer solution includes a diluent.
5. A process according to any preceding claim in which the spraying pressure is from 50 to 300 atmospheres gauge.
6. A process according to any preceding claim in which the surface is the surface of a flowing film of the medium or the smooth parabolic surface of a forced vortex of the medium.
7. A process according to any preceding claim in which the polymer has recurring units of the formula $-\text{Aw}(\text{Ax})_p(\text{Ay})_q(\text{Az})_r-$ where p , q and r may be the same or different and are zero or 1, each radical A is a benzene ring and w , x , y and z which may be the same or different represent direct bonds or $-\text{O}-$ or $-\text{S}-$ atoms or $-\text{SO}_2-$, $-\text{CO}-$, $-\text{CONH}-$, $-\text{N}=\text{N}-$, $-(\text{CH}_2)_n-$ ($n = 1$ or 2) or $-\text{C}(\text{CH}_3)_x-$ groups.
8. A process according to any preceding claim in which the polymer has recurring units of the structure



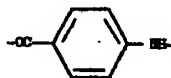
9. A process according to any of claims 1 to 7 in which the polymer has recurring units of the structure



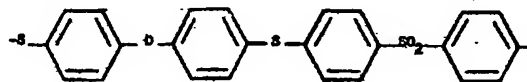
10. A process according to any of claims 1 to 7 in which the polymer has recurring units of the structure



11. A process according to any of claims 1 to 7 in which the polymer has recurring units of the structure



12. A process according to any of claims 1 to 7 in which the polymer has recurring units of the structure



13. A process according to any of claims 1 to 7 in which the polymer is an internal copolymer of 4-mercaptophenol and 4,4'-dichlorodiphenylsulphone with an irregular structural unit.
- 5 14. A process according to claim 1 substantially as herein described with reference to any of the accompanying drawings or with reference to any of the Examples.
15. Powdered polymer obtained by a process according to any preceding claim. 5
- 10 16. Apparatus suitable for use in the process of claim 1 comprising a first supply vessel that may contain the liquid precipitating medium, means in or associated with the first supply vessel for providing a moving surface of the medium, a second supply vessel that may contain the polymer solution, an atomiser nozzle for spraying the solution onto the moving surface and a high pressure pump for delivering the solution to the moving surface. 10
- 15 17. Apparatus according to claim 16 in which the means for providing a moving surface of the medium comprise means for providing a flowing film of the medium or a smooth parabolic surface of a forced vortex of the medium.
18. Apparatus according to claim 16 substantially as herein described with reference to any of the accompanying drawings. 15

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COMPLETE SPECIFICATION

2 SHEETS

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Sheet 1*

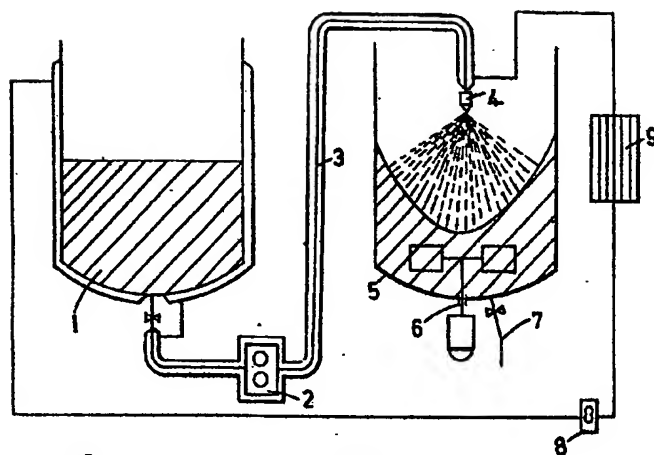


FIG. 1.

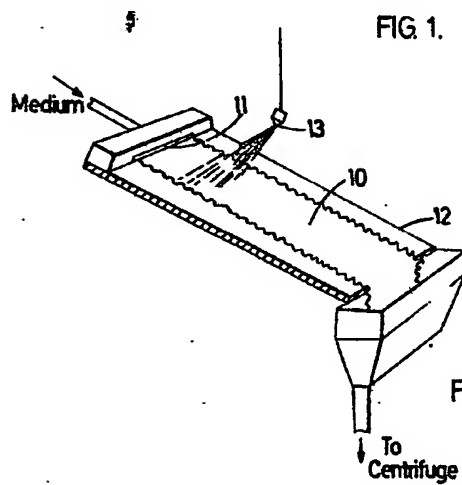


FIG. 2.

